



CATALYTIC OXIDATION OF METHANE OVER Pd-MeO_x (Me = Mn, Co, Ni, Ce) CATALYSTS – INFLUENCE OF METAL OXIDES

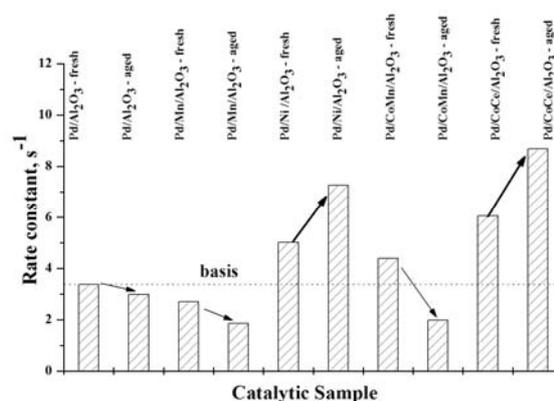
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The activity of Pd/Al₂O₃ catalysts modified with metal oxides (MeO_x; Me = Ni, Co, Ce, Mn) was studied. The catalysts were prepared by sequential impregnation of Al₂O₃ with aqueous solutions of Me(NO₃)₂·6H₂O and Pd(NO₃)₂·2H₂O. All samples were characterized by XRD, TPR and XPS. Results on methane combustion in air show that the catalytic performance of the palladium supported on alumina can be improved significantly by addition of Co, Ni and mixed Co-Ce, Co-Mn oxides. The effect has been attributed to the stabilization of PdO on the catalytic support. The close contact between Pd and Me-oxides could increase the concentration of the surface oxygen species towards the Pd thus leading to stabilization of PdO on the surface. Another factor which increases the catalytic activity in the case of cerium containing sample is the oxygen storage capacity of CeO₂. Ceria may act as oxygen “reservoir” and this is related with dynamic equilibrium between Ce³⁺ and Ce⁴⁺ at reduction/oxidation conditions. The observed low activity of Pd/Mn/Al₂O₃ in comparison with that Pd/Al₂O₃ can be explained by the decrease in the number of active centers after modification with manganese due to possible partial decoration of Pd from manganese oxide. Further, a significant deactivation after aging was observed with the samples promoted with manganese (Pd/Mn/Al₂O₃ and Pd/CoMn/Al₂O₃).



INTRODUCTION

Methane as a greenhouse gas plays a significant role in the global warming.¹ The molecule of methane is characterized as very stable due to its four identical C–H bonds and therefore its oxidation requires an operation at relatively high temperatures and using of catalysts with high activity and thermal stability.^{2,3} Catalytic combustion of methane is achieved by using of noble metal based catalysts, palladium being known to offer a high catalytic activity, however due to the observed deactivation at high temperatures, the efforts of the scientists are directed in searching of new catalysts or further

improvement of the existing catalysts by better dispersion of Pd on catalytically active supports such as pre-modified alumina, hexaaluminates etc.^{4,6} Different metal oxides were tested in the reaction of methane combustion. The following order of activity was established: Co₃O₄ > CuO > NiO > Mn₂O₃ > Cr₂O₃.^{7,8} The metal oxides are a cheaper alternative to noble metals as catalysts for total oxidation, but they are less active at low temperatures.⁹ However, some combinations of oxides may have better thermal stability than noble metals.¹⁰ Sekizawa *et al.*¹¹ and Widjaja *et al.*¹² studying PdO/Al₂O₃–MO_x (where M=Co, Cr, Cu, Fe, Mn and Ni) catalysts observed improvement in the catalytic activity of Mn

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and Ni modified samples. Liu *et al.*¹³ tested Pd/Al₂O₃ catalysts promoted with different metal oxides (Mn, Fe, La, Mg and Ni oxides) and established a remarkable increase in catalytic activity after addition of Ni and Mg. The observed improvement was related to the formation of spinel phase on the support surface. The promising effect of Co on Pd supported on Al₂O₃ catalysts during the methane combustion was observed by Li *et al.*¹⁴ One may suppose that the combination between Pd and different metal oxides should lead to the preparation of promising catalysts in reaction of complete methane.

The present work is aimed at the development of efficient and stable catalysts for methane combustion by study of the effect of different metal oxides (Mn, Ni, Co-Ce, Co-Mn) on Pd/Al₂O₃.

EXPERIMENTAL

Sample preparation

The Pd-based catalysts modified by metal oxide were prepared by sequential impregnation of Al₂O₃ (Rhône-Poulenc (France) spherical particles with diameter 5 – 6 mm, crushed and sieved to fraction 0.3 – 0.6 mm.) with aqueous solutions of Me(NO₃)₂·6H₂O and Pd(NO₃)₂·2H₂O. The Al₂O₃ was first impregnated with aqueous solutions of Me(NO₃)₂·6H₂O (Me=Co, Mn, Ni, Co-Mn, Co-Ce, Me = 5 wt. %). When two oxides (Co-Mn and Co-Ce) were used for modification, the common solutions of respective nitrates were used. After impregnation the samples were dried at 60 °C and calcined for 2 h at 450 °C in air. Palladium (content of about 0.05 %) was introduced on calcined Me/Al₂O₃ samples by impregnation with aqueous solution of Pd(NO₃)₂·2H₂O and then calcined additionally for 2h at 450 °C.

The prepared materials are denoted Pd/Mn/Al₂O₃, Pd/Ni/Al₂O₃, Pd/CoMn/Al₂O₃, Pd/CoCe/Al₂O₃.

Catalysts characterization

Powder X-ray diffraction patterns were collected within the range from 10 to 80 2θ with a constant step of 0.02 2θ on a Bruker D8 Advance diffractometer with Cu Kα radiation and a LynxEye detector. Phase identification was performed with the program X'Pert HighScore.

Temperature programmed reduction (TPR) was carried out using a flow mixture of 10% H₂ in Ar at 10 ml/min, temperature rate of 10 °C/min to 700 °C. Prior to the TPR experiment the samples were treated in Ar for 1 hour at 150°C.

X-ray photoelectron measurements have been carried out on the ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5x10⁻¹⁰ mbar using twin anode MgKα/AlKα X-ray source with excitation energies of 1253.6 and 1486.6 eV, respectively. The spectra are recorded at the total instrumental resolution (as it was measured with the FWHM of Ag3d_{5/2} photoelectron line) of 1.06 and 1.18 eV for MgKα and AlKα excitation sources, respectively. The energy scale has been calibrated by positioning the C1s line of adsorbed adventitious hydrocarbons to 285.0 eV. The processing of the measured spectra includes a subtraction of X-ray satellites and

Shirley-type background.¹⁵ The peak positions and areas are evaluated by a symmetrical Gaussian-Lorentzian curve fitting. The relative concentrations of the different chemical species are determined based on normalization of the peak areas to their photoionization cross-sections, calculated by Scofield.¹⁶

Catalytic tests

Catalytic activity tests were performed using an integrated quartz micro-reactor and mass spectrometer system (CATLAB, Hiden Analytical, UK). The system features: a fast response, low thermal mass furnace with integrated air cooling, a precision Quadrupole Mass Spectrometer, and a quartz inert capillary with “hot zone” inlet for continuous close-coupled catalyst sampling with minimal dead volume and memory effects. The reactant gases (oxygen: 20 Vol.%; methane: 500 ppm; water vapour 1.0 vol. %, balance to 100 %: argon) were supplied through electronic mass flow controllers. The catalysts were held between plugs of quartz wool in a quartz tubular vertical flow reactor (Ø = 6 mm). In order to minimize the external mass transfer limitations the space velocity for the tests was fixed to GHSV = 60 000 h⁻¹ (total gas flow: 24 l/h (STP); the catalyst volume fixed to 0.4 cm³). The gas analysis was performed by CATLAB (Hiden Analytical) instrument equipped with on-line mass-spectrometer. The system features a fast response, low thermal mass furnace with integrated aircooling, a precision Quadrupole Mass Spectrometer for an on-line gas analysis of reactants and products of the reaction. The gas analysis was supplemented by on-line gas-analyzers for CO/CO₂/O₂ (Maihak) and THC-FID (total hydrocarbon content with a flame ionization detector, Horiba).

RESULTS AND DISCUSSION

The XRD data are presented in Fig. 1. The peaks at 2θ = 19.21, 37.38, 45.07, 67.03 and 84.90, belong to the cubic Al₂O₃ (PDF 00-010-0425). Palladium or palladium oxide are not detected in all catalysts revealing finely divided phase of palladium. Despite the low resolved diffraction lines, some information for other oxide phases could be obtained from the diffractograms. The Pd/CoCe/Al₂O₃ exhibits low intensive diffraction peaks corresponding to the CeO₂ (PDF 01-075-0076). The diffraction peaks for Co₃O₄ are not visible, although the broadening of the line at 37.38 can be assumed as a result of the overlap of two peaks – 37.38 originated from [311] plane of Al₂O₃ and 36.86 from [311] plane of Co₃O₄. The shoulder at 2θ = 43.28 in the XRD spectra of Pd/Ni/Al₂O₃ is very likely a result from diffraction peak for NiO phase (PDF 00-022-1189). A broad diffraction lines with low intensity for Co-Mn and Ni-Al mixed oxides appeared in the XRD spectra of Pd/CoMn/Al₂O₃ and Pd/Ni/Al₂O₃ samples. The diffraction peaks are small and relatively broad which makes difficult the identification of the phase. The XRD patterns of Pd/Mn/Al₂O₃ catalysts

reveal the presence of MnO_2 (PDF 01-081-2261, Pyrolusite) and Mn_2O_3 (PDF 00-024-0508, Bixbyite). The Mn_2O_3 and MnO_2 mean crystallite sizes were estimated by application of the Debye–Scherrer equation. The widths of the Mn_2O_3 [222] and MnO_2 [110] peaks at half-maximum were corrected for instrumental broadening. The crystal sizes of the Mn_2O_3 and MnO_2 were 54 and 31 nm, respectively.

Fig. 2 shows H_2 -TPR profiles of all studied samples after calcination. The hydrogen consumption at 70 °C is attributed to the reduction of PdO.^{17,18} The peak with the maximum at 350 °C in the spectrum of Ni modified sample is ascribed to the reduction of NiO. Bulk NiO is reduced at about 400 °C.¹⁹ The shift of the reduction peak to the low temperatures could be result of the particle size effect. The smaller the particle size the lower the registered reduction temperature is.²⁰ The high dispersed and low crystalline NiO particles are confirmed by low resolved XRD pattern for Pd/Ni/ Al_2O_3 catalyst.

H_2 consumption above 500 °C is very likely due to mixed Ni-Al oxide reduction.¹⁶ The XRD reveal the formation of mixed nickel aluminum oxide. One possible explanation for the lack of the reduction peaks in the TPR profile of Pd/CoCe/ Al_2O_3 catalyst is the formation of a strongly interacting with the support cobalt oxide phases (mixed Co-Al or Co-Ce oxides), which are reduced above 700 °C.^{21,22} The reduction maximum for CeO_2 is above 700 °C as well.²³ The TPR spectrum of Pd/CoMn/ Al_2O_3 exhibits maxima in the interval for Co_3O_4 and/or MnO_2 reduction (300–500 °C) and hydrogen consumption at 656 °C. Since both Co_3O_4 and/or MnO_2 oxides are reduced

in the same temperature range, it is very difficult to make a correct assignment regarding first reduction peak. We assume the presence of both Co_3O_4 and MnO_2 on the support as amorphous phases. The lack of XRD diffraction patterns for cobalt and manganese oxides confirms this statement. The reduction peak at 656 °C is ascribed to the mixed Co-Mn oxide reduction.²⁴ This sample was prepared by impregnation of the support with the corresponding nitrates and subsequent calcinations at 450 °C. It has been observed that the decomposition of supported mixed Co–Mn nitrates at low temperatures (250–400 °C) often produces finely divided non-stoichiometric spinels.²¹ In the TPR profile of Pd/Mn/ Al_2O_3 sample three peaks at 347, 408 and 459 °C are visible. The first one can be assigned to the reduction of Mn^{4+} and Mn^{3+} ions to the Mn_3O_4 spinel according to the reduction reactions $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$,^{25–27} while the second may be related to the reduction of Mn_3O_4 to MnO . The small shoulder at 459 °C could be result of the reduction of larger manganese oxide particles.²⁸

The chemical state of Pd, Mn, Co, Ni and the percentage of the different oxidation states of these elements on the catalytic surfaces were studied by X-ray photoelectron spectroscopy. The binding energies of Pd 3d_{5/2} core-level are summarized in Table 1. In order to present a general view on the peak shapes and full widths, the Pd 3d core-level spectra of all catalysts are shown in Fig. 3. The binding energies in the range 336.9–336.2 eV for all studied samples indicate the presence of PdO.^{27,29}

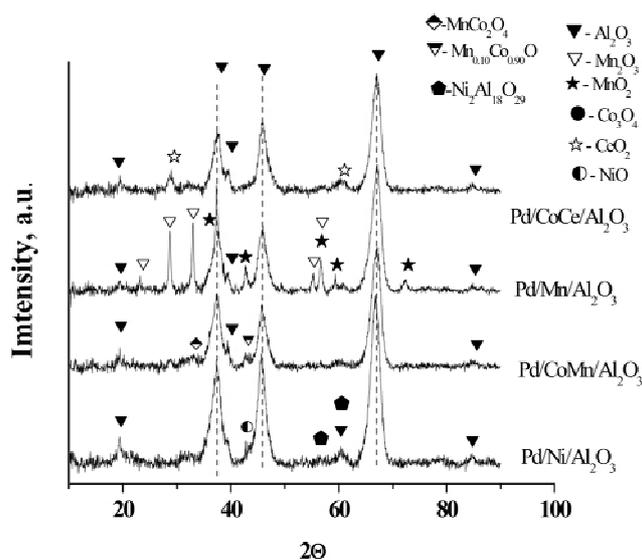


Fig. 1 – XRD patterns of studied catalysts.

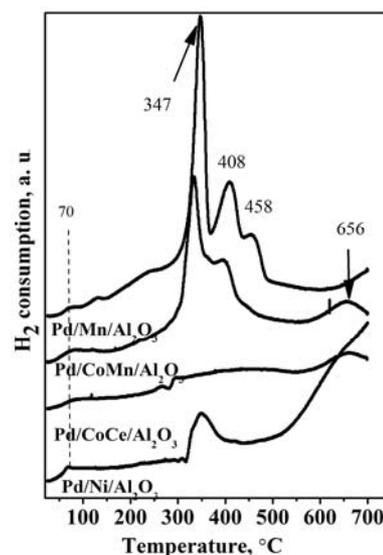


Fig. 2 – TPR profiles of all samples after calcinations.

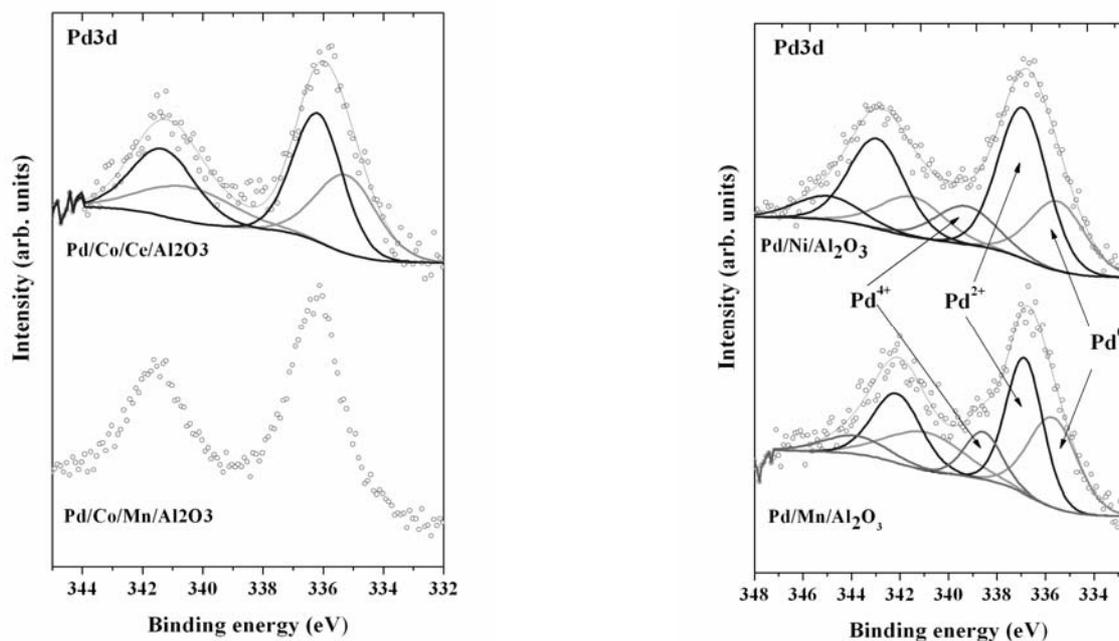


Fig. 3 – Pd 3d core-level spectra of fresh samples.

Table 1

Binding energy and oxidation state of palladium

| Sample | Pd ⁰ % | Pd ⁰ BE (eV) | Pd ²⁺ % | Pd ²⁺ BE (eV) | Pd ⁴⁺ % | Pd ⁴⁺ BE (eV) |
|--|-------------------|-------------------------|--------------------|--------------------------|--------------------|--------------------------|
| Pd/Al ₂ O ₃ | 15 | 334.0 | 85 | 335.8 | | |
| Pd/CoMn/Al ₂ O ₃ | - | - | 100 | 336.2 | | |
| Pd/CoCe/Al ₂ O ₃ | 43 | 335.2 | 57 | 336.2 | | |
| Pd/Mn/Al ₂ O ₃ | 39 | 335.7 | 45 | 336.9 | 16 | 338.6 |
| Pd/Ni/Al ₂ O ₃ | 28 | 335.1 | 55 | 336.3 | 17 | 338.4 |

The binding energies in the interval 335.7–335.1 eV in the photoelectron spectra of Pd/CoCe/Al₂O₃, Pd/Mn/Al₂O₃ and Pd/Ni/Al₂O₃ catalysts are assigned to Pd⁰ species from metal palladium particles. For the Pd/Mn/Al₂O₃ and Pd/Ni/Al₂O₃ a third component at 338.6 eV was observed. It is smaller than the other component detected and contributes with 16% and with 17% of the total Pd signals measured for these two catalysts, respectively. This peak may be associated with Pd⁴⁺ from PdO₂.²⁹ As can be seen from Table 1 and Fig. 3 only Pd²⁺ is observed over Pd/CoMn/Al₂O₃. Palladium in two oxidation state Pd⁰ and Pd²⁺ (ratio Pd⁰/Pd²⁺=0.75) is present at the Pd/CoCe/Al₂O₃ surface. All three oxidation states Pd⁰, Pd²⁺ and Pd⁴⁺ are established over manganese and nickel modified catalysts. The ratio Pd⁰/Pd²⁺ for Pd/Mn/Al₂O₃ is 0.87 and for Pd/Ni/Al₂O₃ – 0.51.

As can be seen from Table 1, the binding energies for Pd⁰ and Pd²⁺ shift to the higher values in the oxide modified samples revealing strong interaction of the small Pd clusters with the support.²⁹

The oxidation state and binding energies of Co and Mn are summarized in Table 2.

Since the differences between the binding energy values of Mn³⁺ and Mn⁴⁺ ions are small, a peak fitting procedure including three components – Mn³⁺, Mn⁴⁺ and a satellite^{31–30} was applied. The observed binding energies at 641.5 eV and 642.9 eV for manganese containing samples are associated with the presence of Mn⁴⁺ and Mn³⁺ ions respectively.^{31–34} The ratio Mn⁴⁺/Mn³⁺ is 1.1 for Pd/Mn/Al₂O₃ catalysts. The Mn⁴⁺ and Mn³⁺ ions are in equal quantity on the surface of sample modified with Co and Mn (Pd/CoMn/Al₂O₃), while the cobalt on the catalytic surface is present in the form of Co²⁺ ions only, as confirmed by the Co 2p_{1/2} peak at 796.9 eV and by comparison with CoO and Co₃O₄ standards.³⁵

The XPS spectrum of the Pd/CoCe/Al₂O₃ sample was fitted assuming that the ratio Co²⁺ to Co³⁺ is equal to 1:2. The Co 2p_{1/2} peak at 795.8 eV indicates the presence of Co³⁺ species.³⁵ The energy positions of the Ce3d peaks and the presence of characteristic peak at 916.5 eV correspond to Ce⁴⁺ in CeO₂,³⁶ suggesting that the presence of cobalt ions does not affect the oxidation state of cerium.

Table 2

Binding energy and oxidation state of Mn and Co

| Sample | Mn ³⁺ % | Mn ³⁺ , BE (eV) | Mn ⁴⁺ % | Mn ⁴⁺ BE (eV) | Co ²⁺ % | Co ²⁺ , BE (eV) | Co ³⁺ % | Co ³⁺ , BE (eV) |
|--|-----------------------|-------------------------------|-----------------------|--------------------------------|-----------------------|-------------------------------|-----------------------|-------------------------------|
| Pd/Mn/Al ₂ O ₃ | 48 | 641.5 | 52 | 642.9 | | | | |
| Pd/CoMn/Al ₂ O ₃ | 50 | 641.6 | 50 | 642.9 | 100 | 796.9 | - | |
| Pd/CoCe/Al ₂ O ₃ | | | | | 76 | 796.9 | 24 | 795.8 |

Table 3

Phase composition and oxidation state of samples

| Sample | Phase composition | Oxidation state of surface species |
|--|---|--|
| Pd/Al ₂ O ₃ | Pd, PdO | Pd ⁰ /Pd ²⁺ =0.18 |
| Pd/CoMn/Al ₂ O ₃ | PdO, amorphous Co ₃ O ₄ and MnO ₂ ; low crystalline MnCo ₂ O ₄ , Mn _{0.1} Co _{0.9} O | Pd ²⁺ , Co ²⁺ , Mn ⁴⁺ /Mn ³⁺ =1.1 |
| Pd/CoCe/Al ₂ O ₃ | Pd, PdO, CeO ₂ , Co ₃ O ₄ , mixed Co-Al or Co-Ce oxides | Pd ⁰ /Pd ²⁺ =0.75, Co ²⁺ /Co ³⁺ =3.1, Ce ⁴⁺ |
| Pd/Mn/Al ₂ O ₃ | Pd, PdO, MnO ₂ , Mn ₂ O ₃ | Pd ⁰ /Pd ²⁺ =0.87, Pd ⁴⁺ , Mn ⁴⁺ /Mn ³⁺ |
| Pd/Ni/Al ₂ O ₃ | Pd, PdO, NiO, Ni-Al mixed oxides | Pd ⁰ /Pd ²⁺ =0.5, Pd ⁴⁺ , Ni ²⁺ |

The Ni 2p spectra (not given here) of Ni doped sample are characterized by two main lines of Ni 2p_{3/2} and Ni 2p_{1/2} with maxima at about 856.5 eV and 873 eV, respectively; each having an intensive shake-up satellite at higher binding energy.³⁷ The doublet Ni2p spectra and peak binding energy values suggest that nickel is mainly present as Ni²⁺ on the sample surface.

The phase composition and oxidation state of all samples are summarized in Table 3.

The temperature dependences of the complete methane oxidation over mono and two component catalysts are shown in Fig. 4. H₂O and CO₂ were the only detectable reaction products on all studied samples. Experiments on thermal treatment (ageing) for 120 h at 505 °C were also performed aim to test the catalysts according to their thermal stability. The order of activity is the following: Pd/CoCe/Al₂O₃ > Pd/CoMn/Al₂O₃ > Pd/Ni/Al₂O₃

≅ Pd/Al₂O₃ > Pd/Mn/Al₂O₃. As can be seen the addition of Co, Ce, Ni and Mn improve significantly the catalytic activity. This effect could be explained with stabilization of Pd and PdO on the support on the oxide modified catalysts. As was established by XRD and XPS the addition of different oxides on the alumina promote the formation of small Pd and PdO clusters. Liu *et al.*¹³ demonstrated that the addition of NiO inhibited the sintering of palladium particles in PdNiAl catalyst because of the formation of NiAl₂O₄ phase. The strong interaction between NiAl₂O₄ and Pd particles restricts the migration of Pd particles and effectively stabilizes the Pd particles with low crystallite size. According Li *et al.*,⁷ the cobalt improves methane combustion of Pd/Al₂O₃ catalysts and this is depends of CoAl₂O₄/Co₃O₄ ratio.

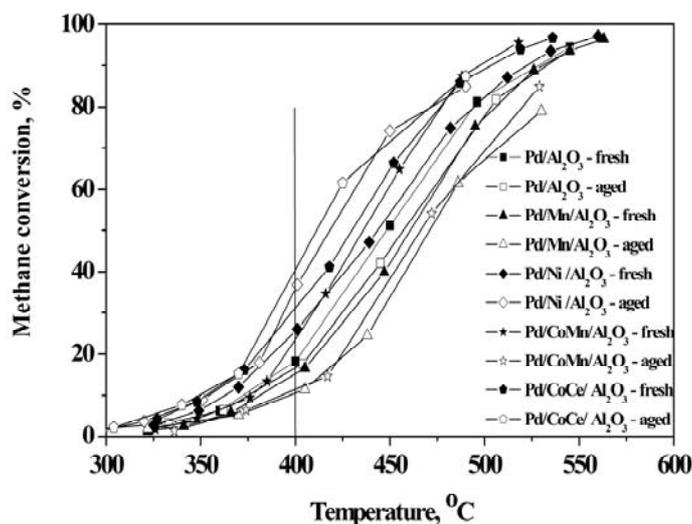


Fig. 4 – Conversion vs. temperature in the reaction of complete methane oxidation for fresh and aged samples.

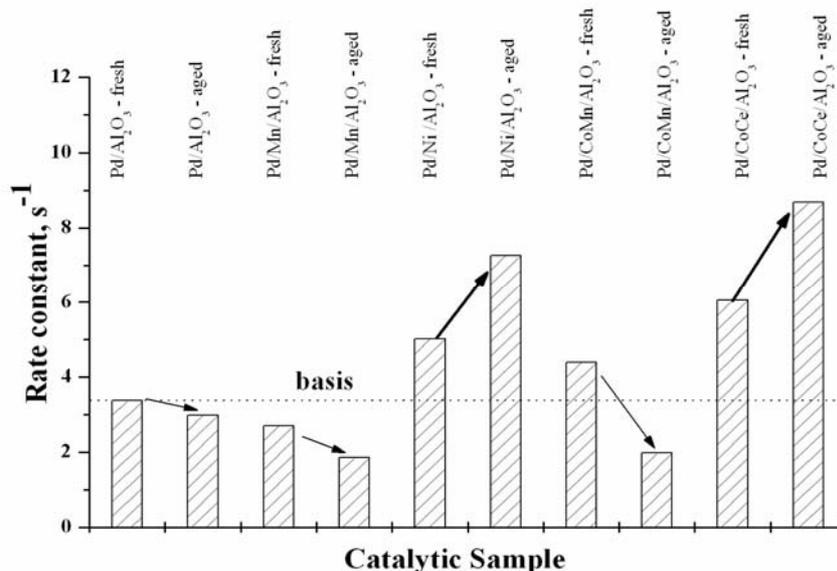


Fig. 5 – Comparative data for the rate constants calculated for fresh and aged samples.

The temperature of 400 °C was chosen for comparative analysis of the reaction rates due to the range of observed relatively low conversions, typical for the chemical reaction control. The calculated rate constants assuming first order kinetics (detailed kinetics investigation to be subject of further study) are not affected by the diffusion restrictions which could be useful for comparative analysis of the specific activities of the samples. For example, the ratio $k_i/k_{Pd-fresh}$ provides information for the effect of modifying and ageing procedures on the specific activities of the samples when compared with the basis sample of fresh Pd/Al₂O₃. Its value also shows the extent of this effect – obviously the most stable is unmodified Pd/Al₂O₃, the lowest stability being observed with Pd/CoMn/Al₂O₃. Further, the ratio $k_{i,aged}/k_{i,fresh}$ within samples from the same catalyst shows the differences in the pre-exponent due to ageing process. The lower than unity $k_{Pd/Mn}/k_{Pd-fresh}$ – ratio indicates that the modification with manganese decreases significantly the reaction rate. However, in two of the cases the ratio $k_{i,aged}/k_{i,fresh}$ is higher than unity which shows an activation after the thermal treatment. The reasons for this phenomenon need deeper consideration and will be task to the future experimental investigations.

In our previous studies we established that the catalysts prepared by common solution of Co- Mn and Ce nitrates^{21, 23} manifested a considerable increase in activity during *n*-hexane combustion whose effect was explained with the very low crystallinity of the supported metal oxide phases,

partial enrichment of the surface with cobalt and more uniform distribution of oxide agglomerates on the support. A formation of finely divided cobalt, manganese, Co-Mn, Co-Ce and Ni-Al mixed oxides on the surface of Pd/CoCe/Al₂O₃, Pd/CoMn/Al₂O₃ and Pd/Ni/Al₂O₃ catalysts is evident from XRD and TPR studies. As result of the low crystallinity of these oxides on the surface,^{38,39} an enrichment of the surface with oxygen species for all oxides modified samples could be expected. According to Morales³⁸ the vacancies from structural defects associated with the poor crystallinity of the oxide can ensure adsorption centres for oxygen. The close contact between Pd and oxides could result in supply of more oxygen to Pd thus stabilizing it on the support in form of PdO. Another factor which increases catalytic activity of the cerium containing sample is the oxygen storage capacity of ceria – it may acts as oxygen “reservoir” and this is related with the reduction/oxidation equilibrium between Ce³⁺ and Ce⁴⁺.

A deactivation process was observed with the Mn – containing samples Pd/Mn/Al₂O₃ and Pd/CoMn/Al₂O₃. A tentative explanation of this behavior could be related to the decrease in the catalytic active centers as a possible partial decoration of Pd from manganese oxide.⁴⁰

CONCLUSIONS

Based on the results obtained the following conclusions can be made:

The catalytic performance of the catalysts based on palladium supported on alumina can be improved significantly by addition of metal oxides of Ni, Co and mixed Co – Ce, Co-Mn oxides whose effect has been attributed to the formation of high dispersed well stabilized Pd or PdO clusters on the support, thus increasing the catalytic activity.

The close contact between Pd and oxides could result in supply of more oxygen to Pd thus stabilizing it on the support in form of PdO.

The activation after the thermal treatment is observed for Pd/CoCe/Al₂O₃, and Pd/Ni/Al₂O₃ samples.

Remarkable deactivation proceeds when the samples are modified with Mn - oxides (Pd/Mn/Al₂O₃ and Pd/CoMn/Al₂O₃). The decrease in the number of active centers might be due to partial decoration of Pd from manganese oxide.

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